भारतीय मानक

Indian Standard

IS 3025 (Part 36) : 2023

जल एवं अपशिष्ट जल के नमूने लेने और परीक्षण (भौतिक एवं रसायनिक) की पद्धतियाँ

भाग 36 ओजोन, अवशिष्ट

(दूसरा पुनरीक्षण)

Methods of Sampling and Test (Physical and Chemical) for Water and Wastewater

Part 36 Ozone, Residual

(Second Revision)

ICS 13.060.50

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भारतीय मानक ब्यूरो
BUREAU OF INDIAN STANDARDS
मानक भवन, 9 बहादुर शाह ज़फर मार्ग, नई दिल्ली - 110002
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI - 110002
www.bis.gov.in www.standardsbis.in

December 2023 **Price Group 5**

Water Quality Sectional Committee, CHD 36

FOREWORD

This Indian Standard (Second Revision) was adopted by the Bureau of Indian Standards, after the draft finalized by the Water Quality Sectional Committee had been approved by the Chemical Division Council.

Ozone is a strong oxidant and an excellent disinfectant. Ozone is used at water treatment plants throughout the world to address disinfection, disinfection by-products, taste and odour, colour, micro-coagulation, and other water treatment needs. Ozone can effectively destroy bacteria and inactive viruses more rapidly than any other disinfectant chemical. Ozone reacts to oxidize a number of inorganic compounds including iron, manganese, sulphides, nitrite, arsenic, bromide ion, and iodide ion. Iron and manganese can be reduced to very low, safe levels in water supplies through ozone oxidation. This same process is used to liberate organically bound heavy metals, which otherwise are not easily removed.

However, ozone is toxic, the toxicity being proportional to its concentration and exposure time. Thus, it is important to monitor the residual ozone in water and wastewater after treatment with ozone.

The Committee responsible for formulation of IS 3025 : 1964 'Methods of sampling and test (physical and chemical) for water used in industry' decided to revise the standard and publish it in separate parts. This standard was one among the different parts published under IS 3025 series of standards. The first revision of this standard was published in 1987.

In this revision the following changes have been incorporated:

a) Indigo colorimetric method has been incorporated;

b) References, ICS No. have been updated; and

c) Other editorial changes have been done to bring the standard in the latest style and format of Indian Standards.

There is no ISO standard on this subject area. In the preparation of this standard, considerable assistance has been derived from the methods 4500-O_3 B of — Standard methods for the examination of water and wastewater, published by the American Public Health Association, Washington, USA, 23rd edition, 2017.

The composition of the Committee responsible for formulation of this standard is given in Annex A.

In reporting the results of a test or analysis in accordance with this standard, if the final value observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 2022 'Rules for rounding off numerical values (*second revision*)'.

Indian Standard

METHODS OF SAMPLING AND TEST (PHYSICAL AND CHEMICAL) FOR WATER AND WASTE WATER

PART 36 OZONE, RESIDUAL

(Second Revision)

1 SCOPE

This standard (Part 36) prescribes the following methods for determination of ozone, residual in water and wastewaters:

a) Titrimetric method (minimum detectable concentration by this method is 30 µg/l); and

b) Indigo colorimetric method (practical lower limit for residual concentration is 10 µg/l to 20 µg/l).

2 REFERENCES

The standards given below contain provisions which through reference in this text constitute provisions of this standard. At the time of publications, the editions indicated were valid. All standards are subject to revision and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of these standards:

IS No.	*Title*
IS 2263 : 1979	Methods of preparation of indicator solutions (*first revision*)
IS 7022 (Part 1) : 1973	Glossary of terms relating to water, sewage and industrial effluents: Part 1
IS 7022 (Part 2) : 1979	Glossary of terms relating to water, sewage and industrial effluents: Part 2

3 TERMINOLOGY

For the purpose of this standard, the definitions given in IS 7022 (Part 1) and IS 7022 (Part 2) shall apply.

4 TITRIMETRIC METHOD

4.1 Principle

Ozone liberates iodine from potassium iodide solution. After immediate acidification, the liberated iodine is titrated with standard sodium thiosulphate with starch as indicator.

4.2 Interference

Ozonated water may contain manganese dioxide, ferric ion, chlorine, nitrite, peroxide and other oxidation products. Avoid their interference by passing ozone through the gaseous phase into potassium iodide solution for titration. The stability of ozone solution decreases progressively at increment in temperature above freezing and with each increment in *p*H above 3.0. The minimum detectable concentration by this method is 30 µg/l.

4.3 Apparatus

4.3.1 *Gas-washing Bottles and Absorbers* — 1 000 ml and 500 ml capacities.

4.3.2 *Pure Air or Nitrogen Supply* — 0.2 litre/min to 1.0 litre/min capacity.

4.3.3 *Glass, Stainless Steel or Aluminium, Piping*, for carrying ozonized air (good quality PVC tubes may be used for short runs but not rubber).

4.4 Reagents

4.4.1 *Potassium Iodide Solution*

Dissolve 20 g of potassium iodide, free from iodate and reducing agents in 1 litre of freshly boiled and cooled water. Store in a brown bottle in refrigerator.

4.4.2 *Sulphuric Acid* — 1 N

4.4.3 *Standard Sodium Thiosulphate* — 0.1 M

Dissolve 25 g of sodium thiosulphate ($Na_2S_2O_3.5H_2O$) in 1 litre freshly boiled distilled water. Standardize against potassium hydrogen iodate or potassium dichromate.

4.4.4 *Standard Sodium Thiosulphate* — 0.005 M

Dilute proper volume (about 50 ml) of 0.1 M solution (**4.4.3**) to 1 000 ml. For accurate work, standardize this also against potassium hydrogen iodate or potassium dichromate.

4.4.5 *Starch Indicator Solution*

Prepare as given in IS 2263.

4.4.6 *Standard Iodine Solution* — 0.1 M

Dissolve 40 g of potassium iodide in 25 ml of distilled water. Add 13 g of resublimed iodine and stir until dissolved. Dilute to one litre and standardize against arsenite solution.

4.4.7 *Standard Iodine Solution* — 0.005 M

Dissolve 16 g of potassium iodide in little distilled water in a 1 litre volumetric flask, add proper volume of 0.1 M iodine solution and dilute to mark. For accurate work, standardize daily. Store in a brown bottle or in the dark. Protect from direct sunlight and keep from contact with rubber.

4.5 Procedure

4.5.1 *Sample Collection*

Collect an 800 ml sample in a 1 litre gas washing bottle. Pass stream of pure air or nitrogen through the sample and through an absorber containing 400 ml of potassium iodide solution. Continue for 5 min to 10 min at a rate of 0.2 l/min to 1.0 l/min to insure that all ozone is swept from the sample and absorbed in potassium iodide solution.

4.5.2 *Titration*

Transfer potassium iodide solution to a 1 litre beaker, rinse absorber and add 20 ml of 1 N sulphuric acid to reduce *p*H below 2.0. Titrate with 0.005 M sodium thiosulphate titrant until yellow colour of liberated iodine is almost is discharged. Add 4 ml of starch indicator solution and continue titrating carefully but rapidly to the end point, at which the blue colour just disappears. Long contact of iodine and starch develops a blue compound that is difficult to decolorize.

4.5.3 *Blank Test*

Correct sample titration result by determining black contributed by such reagent impurities as free iodine or iodate in potassium iodide or traces of reducing agents that might reduce liberated iodine.

4.5.4 Take 400 ml of potassium iodide solution, 20 ml of 1 N sulphuric acid and 4 ml of starch indicator solution.

Perform whichever of the following blank titration is applicable:

a) If a blue colour appears, titrate with 0.005 M sodium thiosulphate to disappearance of blue and record result; and
b) If no blue colour appears, titrate with 0.005 M iodine solution until a blue colour appears. Back titrate with 0.005 M sodium thiosulphate to disappearance and record the difference.

Before calculating ozone concentration, subtract blank titration from (a) above from sample titration, or add result of (b) above.

4.6 Calculation

$$\text{Ozone (residual) as } O_3\text{, mg/l} = \frac{(A - B) \times \mathrm{M} \times 24\,000}{V}$$

where

A = volume of titrant for sample, in ml;

B = volume of titrant for blank, in ml;

M = molarity of thiosulphate; and

V = volume of sample used in the test, in ml.

5 INDIGO COLORIMETRIC METHOD

5.1 Principle

Ozone rapidly decolorizes indigo, in acidic solution. Absorbance decreases linearly with increase in concentration. The proportionality constant at 600 nm is 0.42 cm/mg/l ± 0.01 cm/mg/l compared to the ultraviolet absorption of pure ozone of E = 2 950/M cm at 258 nm.

5.2 Interference

Hydrogen peroxide (H_2O_2) and organic peroxides decolorizes the indigo reagents very slowly. H_2O_2 does not interfere if ozone is measured in less than 6 h after adding reagents. Organic peroxides may react more rapidly. Fe (III) does not interfere. Mn (II) does not interfere but it is oxidized by ozone to form ozonated manganese that decolorize the reagent. Correct for this decolourization by making the measurements relative to a blank in which the ozone has been destroyed selectively. Without the corrective procedure, 0.1 mg/l ozonated manganese gives a response of about 0.08 mg/l apparent ozone. Chlorine also interferes. Low concentration of chlorine (< 0.1 mg/l) can be masked by melonic acid. Hydrobromous acid, which can be formed by oxidation of bromine interferes. In the presence of hydrobromous acid or chlorine in excess of 0.1 mg/l, an accurate measurement of ozone cannot be made with this method. The practical lower limit of residual measurement is 10 µg/l to 20 µg/l.

5.3 Apparatus

Spectrophotometer for use at 600 nm ± 10 nm.

5.4 Reagents

5.4.1 *Indigo Stock Solution*

In a 1 litre volumetric flask add 500 ml distilled water and 1 ml concentrated phosphoric acid and. Stir it well. Add 770 mg potassium indigo trisulphonate, ($C_{16}H_7N_2O_{11}S_3K_3$) (use only high-grade reagent commercially available at about 80 percent to 85 percent purity) and continue stirring. Add the distilled water to the mark. A 1 : 100 dilution exhibits an absorbance of 0.2 cm ± 0.01 cm at 600 nm. The stock solution is stable for about 4 months when stored in the dark. The 1 : 100 dilution to be discarded when absorbance falls below 0.16 cm. Do not change concentration of dye for higher ranges of ozone residual. Volume of dye used may be adjusted.

5.4.2 *Indigo Reagent* I

To a 1 litre volumetric flask, add 20 ml indigo stock solution, 10 gm Sodium di-hydrogen phosphate (NaH_2PO_4) and 7 ml concentrated phosphoric acid. Add distilled water up to the mark. Typically within a week check if absorbance has been decreased to less than 80 percent of its initial value, prepare a fresh solution.

5.4.3 *Indigo Reagent* II

Proceed as with indigo reagent I, but add 100 ml indigo stock solution instead of 20 ml.

5.4.4 *Malonic Acid Reagent*

Dissolve 5 gm malonic acid in water and dilute to 100 ml.

5.4.5 *Glycine Reagent*

Dissolve 7 gm glycine in water and dilute to 100 ml.

5.5 Procedure

5.5.1 *Spectrophotometric*, *Volumetric Procedure*

5.5.1.1 *Concentration range 0.01 mg* O_3*/l to 0.1 mg* O_3*/l*

Add 10 ml indigo reagent I to each of two 100 ml volumetric flasks. Fill one flask (blank) to mark with distilled water. Fill other flask to mark with sample. Measure absorbance of both solutions at 600 nm ± 10 nm as soon as possible but at least within 4 h. Preferably use 10 cm cells. Calculate the ozone concentration from the difference between the absorbance found in sample and blank.

5.5.1.2 *Concentration range 0.05 mg* O_3*/l to 0.5 mg* O_3*/l*

Proceed as above (**5.5.1.1**) using 10 ml indigo reagent II instead of indigo reagent I. Absorbance is preferably measured in 4 cm or 5 cm cells.

5.5.1.3 *Concentration greater than 0.3 mg* O_3/l

Proceed using indigo reagent II (**5.4.3**), but for these higher ozone concentrations, use a correspondingly smaller sample volume. Dilute resulting mixture to 100 ml with distilled water.

5.5.2 *Spectrophotometric*, *Gravimetric Procedure*

5.5.2.1 To 100 ml volumetric flask (blank), add 10 ml indigo reagent II (**5.4.3**). Now add distilled water to flask to the mark. Determine tare weight of a second flask (volumetric or Erlenmeyer). To this second flask add 10 ml indigo reagent II. Fill directly with sample (do not run water down side) and swirl second flask until blue solution has turned to a light blue colour. Weigh flask containing indigo and sample.

5.5.2.2 Preferably using 10 cm. cells, measure absorbance of both solutions at 600 nm ± 10 nm. as soon as possible, but at least within 4 h. A maximum delay of 4 h before spectrophotometric reading is suitable only for drinking water samples. For other sample types, test the time drift.

5.6 Calculation

a) Spectrophotometric, volumetric method, mg

$$O_3/l = \frac{100 \times €A}{f \times b \times V}$$

where

$€A$ = difference in absorbance between sample and blank;
f = 0.42;
b = path length of cell, in cm; and
V = volume of sample (normally 90 ml), in ml.

b) Spectrophotometric, gravimetric method,

$$\text{mg } O_3/\text{l} = \frac{(A \times 100) - (B \times C)}{f \times D \times b}$$

where

A = absorbance of blank;

B = absorbance of sample;

f = 0.42;

D = volume of sample, in ml = {final weight – tare weight) × g × 1.0 ml/g} – 10.0 ml;

C = total volume of sample plus indigo, in ml = (final weight – tare weight) g × 1.0 ml/g; and

b = path length of cell, in cm.

ANNEX A

(*Foreword*)

COMMITTEE COMPOSITION

Water Quality Sectional Committee, CHD 36

Organization	*Representative(s)*
Chief Scientist, EPTRI, Hyderabad	Shri N. Raveendhar **(*Chairperson*)**
Andhra Pradesh Pollution Control Board, Vijaywada	Shrimati M. Sreeranjani Shrimati A. Sri Samyuktha (*Alternate*)
Bhabha Atomic Research Centre, Mumbai	Dr S. K. Sahu Shri I. V. Saradhi (*Alternate*)
Central Institute of Mining and Fuel Research, Dhanbad	Dr Abhay Kumar Singh
Central Pollution Control Board, New Delhi	Shri P. K. Mishra Shri Vishal Gandhi (*Alternate*)
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Envirocare Laboratories Pvt Ltd, Thane	Dr Priti Amritkar Shri Nilesh Amritkar (*Alternate*)
Bureau of Indian Standards, New Delhi	Ms Nitasha Doger
Gujarat Pollution Control Board, Gandhinagar	Dr D. N. Vansadia Shri K. B. Vaghela (*Alternate*)
Haryana State Pollution Control Board, Panchkula	Shri Jatinder Pal Singh
Himachal Pradesh State Pollution Control Board, Governemnt of Himachal Pradesh, Shimla	Er Praveen Gupta Shri Praveen SHARMA (*Alternate*)
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Indian Water Works Association, New Delhi	Shri Vijay Charhate
Karnataka State Pollution Control Board, Bengaluru	Dr H. Rupadevi Ms Gouri Golsangi (*Alternate*)

Organization	*Representative(s)*
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Ministry of Jal Shakti Department of Drinking Water and Sanitation, New Delhi	SHRI D. A. RAJASEKHAR SHRI SUMIT PRIYADARSHI (*Alternate*)
National Environmental Engineering Research Institute, Nagpur	DR NOOR A. KHAN
National Institute of Oceanography, Vishakhapatnam	DR V. V. S. S. SARMA DR DURBAR RAY (*Alternate*)
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Shriram Institute for Industrial Research, New Delhi	DR VIVEK NARAYAN SINGH DR JAGDISH KUMAR (*Alternate*)
Telangana State Pollution Control Board, Hyderabad	DR M. S. SATYANARAYANA RAO
Uttar Pradesh Pollution Control Board, Lucknow	DR ARUNIMA BAJPAI
In Personal Capacity (*1221, Mahatma Gandhi Road, P. O. - Haridevpur, Kolkata - 700082*)	SHRI SANJIB KUMAR GOSWAMI
In Personal Capacity (*S-168 A- Uppal Sothend, Sector 49, Sohna Road, Gurugram - 122018*)	SHRI RAKESH MALHOTRA
In Personal Capacity (*H. No. 1-78/2/S/121/1, Sathi Reddy nagar colony, Boduppal, Hyderabad - 500092*)	SHRI N. MURALI MOHAN
In Personal Capacity (*Z-7, 1st Floor, Sector 12, Noida-201301*)	SHRI S. N. A. RIZVI
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Member Secretary

MS SHUBHANJALI UMRAO
SCIENTIST ‘B’/ASSISTANT DIRECTOR
(CHEMICAL), BIS

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BUREAU OF INDIAN STANDARDS

Headquarters:

Manak Bhavan, 9 Bahadur Shah Zafar Marg, New Delhi 110002
Telephones: 2323 0131, 2323 3375, 2323 9402 *Website*: www.bis.gov.in

Regional Offices: *Telephones*

Central : 601/A, Konnectus Tower -1, 6th Floor, DMRC Building, Bhavbhuti Marg, New Delhi 110002 — 2323 7617

Eastern : 8th Floor, Plot No 7/7 & 7/8, CP Block, Sector V, Salt Lake, Kolkata, West Bengal 700091 — 2367 0012, 2320 9474

Northern : Plot No. 4-A, Sector 27-B, Madhya Marg, Chandigarh 160019 — 265 9930

Southern : C.I.T. Campus, IV Cross Road, Taramani, Chennai 600113 — 2254 1442, 2254 1216

Western : Plot No. E-9, Road No.-8, MIDC, Andheri (East), Mumbai 400093 — 2821 8093

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